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Office européen des brevets



(11) Publication number: **0 372 388 B1**

(12)

EUROPEAN PATENT SPECIFICATION

- (43) Date of publication of patent specification: 16.02.94 (51) Int. Cl.⁵: **D21H 17/43, D21H 17/37, D21H 17/26**
- (21) Application number: 89122081.6
- (22) Date of filing: 30.11.89

(54) **Water-disintegrable cleaning sheet.**

- (20) Priority: 30.11.88 JP 303159/88
30.11.88 JP 303160/88
28.02.89 JP 47534/89

- (43) Date of publication of application:
13.06.90 Bulletin 90/24

- (45) Publication of the grant of the patent:
16.02.94 Bulletin 94/07

- (64) Designated Contracting States:
AT BE DE ES FR GB IT NL

- (56) References cited:
EP-A- 0 013 969
EP-A- 0 112 654

DATABASE WPIL, DERWENT PUBLICATIONS,
LONDON, GB, ACCESSION NUMBER:
87-040240

DATABASE WPIL, DERWENT PUBLICATIONS,
LONDON, GB, ACCESSION NUMBER:
88-101397

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Description**FIELD OF THE INVENTION**

6 This invention relates to a water-disintegrable cleaning sheet, and more particularly to a water-disintegrable cleaning sheet comprising a specific water disintegrable paper having incorporated or impregnated there into an aqueous cleaning agent containing an organic solvent, which is suitable for cleaning or sterilization of floors or walls of rooms or toilet rooms, furniture, toilet seats, toilet basins, etc. or useful as toilet paper, and can be thrown into flushing water.

10 **BACKGROUND OF THE INVENTION**

Water-disintegrable papers or cleaning goods made of a chemical-containing water-disintegrable paper which can be thrown into water have been used as toilet paper or for cleaning a toilet room or toilet equipment. Conventional water-disintegrable paper usually contains a dry strength agent such as polyvinyl alcohol, carboxymethyl cellulose, and cationic starch, for enhancing dry paper strength without impairing water disintegrability.

However, a paper sheet containing a dry strength agent undergoes serious reduction of strength when impregnated with water. Therefore, where a water-disintegrable paper is combined with a cleaning agent for cleaning or sterilization of floors, walls, furniture, and toilet equipment or for use as toilet paper, the cleaning agent to be combined with has been limited to liquid substances or chemicals having no or very low water content.

In using a cleaning agent of high water content, it has been necessary that the cleaning agent should be foamed and sprayed on a water-disintegrable paper immediately before use and be used without delay in order to suppress water absorption into paper and to prevent strength reduction.

Polyacrylamide or the like dry strength agent endows paper with strength enough to withstand use even with a small amount of water being impregnated in the paper sheet, but tends to impair water disintegrability of the sheet.

Hence, the conventional dry strength agents could not provide a strength enough to withstand cleaning use even when combined with a cleaning agent of high water content in good balance with water disintegrability.

It has been proposed to spray a binder solution containing polyvinyl alcohol and borax on a paper sheet followed by drying by heat whereby polyvinyl alcohol and borax are reacted to provide water-disintegrable paper having temporary water resistance, which is useful as absorbent materials such as napkin or diaper, as disclosed in JP-A-47-9486 (the term "JP-A" as used herein means an "unexamined published Japanese patent application"). Further, JP-A-61-296159 discloses a water-disintegrable paper in which an aqueous solution containing salts such as potassium salt, calcium salt and barium salt, is impregnated into a fibrous sheet containing carrageenan as a binder, which is used for a wetting tissue paper. Furthermore, JP-A-55-103393 discloses a method for preparing a paper having high strength in a dry state while low in wet state, which comprises treating paper surface with alkali metal and/or alkali earth metal salt of polyacrylic acid polymers, and that the paper can be used for writing paper, printing paper, wrapping paper, etc. These water-disintegrable papers, however, does not withstand the mechanical force in cleaning work when impregnated with water.

EP-A-112 654 discloses a flexible sheet-like article, for example, for wiping hard surfaces, comprising first and second sheet substrates, at least one of which is liquid-permeable, having sandwiched between them an intermediate layer of solid core material comprising absorbent and/or active material.

SUMMARY OF THE INVENTION

50 An object of the present invention is to provide a water-disintegrable cleaning sheet containing a cleaning agent, which has strength enough for cleaning use under a mechanical force while retaining satisfactory water disintegrability.

As a result of extensive investigations, the inventors have found that the above object of the present invention is accomplished by incorporating a water-soluble binder having a carboxyl group and at least one metallic ion selected from the group consisting of ions of an alkaline earth metal, manganese, zinc, cobalt and nickel, and an aqueous cleaning agent containing an organic solvent into a web composed of water-dispersible fibers.

The present invention provides a water-disintegrable cleaning sheet comprising a web of water-dispersible fibers having incorporated therein a water-soluble binder having a carboxyl group; at least one polyvalent metallic ion selected from the group consisting of ions of alkaline earth metals, zinc, cobalt and nickel; and an aqueous cleaning agent containing an organic solvent.

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DETAILED DESCRIPTION OF THE INVENTION

Water-dispersible fibers which constitute a water-disintegrable cleaning sheet of the present invention are not particularly restricted as long as they are fibrous materials substantially dispersible in water. Examples of suitable water-dispersible fibers are wood pulp fibers, non-wood vegetable fibers, and synthetic fibers such as rayon fibers and polyester fibers.

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Water-soluble binders having a carboxyl group which can be used in the present invention include polysaccharide derivatives, synthetic high polymers, and naturally-occurring substances.

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Examples of suitable polysaccharide derivatives include carboxymethyl cellulose, carboxyethyl cellulose, and carboxymethylated starch, with carboxymethyl cellulose being preferred.

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Examples of suitable synthetic high polymers include homopolymers of an unsaturated carboxylic acid, copolymers of two or more unsaturated carboxylic acids, and copolymers of an unsaturated carboxylic acid and other copolymerizable monomer. Specific examples of suitable unsaturated carboxylic acids are acrylic acid, methacrylic acid, itaconic acid, crotonic acid, maleic anhydride, maleic acid, and fumaric acid. Monomers copolymerizable with the unsaturated carboxylic acid include esters of these unsaturated carboxylic acids, vinyl acetate, olefins (e.g., ethylene), acrylamide, and vinyl ether. Preferred of these high polymers are those containing an acrylic acid and/or methacrylic acid unit, e.g., polyacrylic acid, polymethacrylic acid, an acrylic acid-methacrylic acid copolymer, and an acrylic acid (or methacrylic acid)-alkyl acrylate (or alkyl methacrylate) copolymer.

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Examples of suitable naturally-occurring water-soluble binders are alginic acid, xanthan gum, arabic gum, tragacanth gum, and pectin.

Among these water-soluble binders, carboxymethyl cellulose is particularly preferred.

The water-soluble binder is usually used in an amount of from 0.1 to 30% by weight, preferably from 1 to 15% by weight, and more preferably from 1 to 10% by weight, based on an amount of a dry web.

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A metallic ion which is incorporated into the water-disintegrable cleaning sheet of the present invention (hereinafter referred to as an "essential metallic ion") is at least one selected from the group consisting of ions of alkaline earth metals such as magnesium, calcium, strontium and barium; manganese; zinc; cobalt; and nickel.

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Of the metallic ions as described above, calcium, strontium, barium, zinc, cobalt, and nickel ions are preferred from the standpoint of sufficient strength for cleaning work of the cleaning sheet of the present invention.

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Monovalent metallic ions other than those described above satisfy water disintegrability but cannot afford strength withstanding cleaning work. Divalent metallic ions other than those described above, e.g., Cu^{2+} , Fe^{2+} or Sn^{2+} , and trivalent metallic ions other than those described above, e.g., Fe^{3+} or Al^{3+} , afford strength enough for cleaning work but do not satisfy water disintegrability.

The essential metallic ion is preferably used in an amount of at least 1/4 mol, more preferably at least 1/2 mol, per mol of carboxyl group of the water-soluble binder.

The essential metallic ion is incorporated into the water-disintegrable cleaning sheet of the present invention in the forms:

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(A) an intermolecular mixed salt of the water-soluble binder formed between the carboxyl group thereof and (a) an alkali metal and (b) at least one selected from the group consisting of alkaline earth metals, manganese, zinc, cobalt and nickel; and/or

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(B) at least one of water-soluble salts such as hydroxides, chlorides, sulfates, nitrates, carbonates, formates and acetates, of at least one selected from the group consisting of an alkaline earth metal, manganese, zinc, cobalt and nickel.

In the intermolecular mixed salt as mentioned above as form (A), a molar ratio of (a)/(b) is in the range of from 1/0.01 to 1/10, preferably from 1/0.05 to 1/3.

When the metal ion is incorporated into the cleaning sheet of the present invention in the form (B) above, an alkali metal salt of the binder which formed a salt between the carboxyl group and an alkali metal such as sodium and potassium, is preferably used as a water-soluble binder.

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The above forms (A) and (B) of the essential metallic ion are used each alone, or combination thereof to incorporate the essential metallic ion into the cleaning sheet of the present invention.

The water-disintegrable cleaning sheet of the present invention can be produced by incorporating water-disintegrable paper composed of the above-mentioned components with an aqueous cleaning agent containing an organic solvent.

Processes for producing the water-disintegrable paper which constitute the water-disintegrable cleaning sheet of the present invention are not particularly restricted and include conventionally known wet process and dry process. For example, when the essential metallic ion is incorporated in the water-disintegrable paper in the form (B) above, the water-disintegrable paper can be obtained by spraying or coating an aqueous solution of the water-soluble salt of at least one selected from the group consisting of alkaline earth metals, manganese, zinc, cobalt and nickel, to a dry web containing carboxyl-containing water-soluble binder, and then drying. The paper containing carboxyl-containing water-soluble binder is obtained by adding a carboxyl-containing water-soluble binder into an aqueous dispersion of water-dispersible fibers and then subjecting paper making, or by spraying or coating a carboxyl-containing water-soluble binder to a web composed of water-dispersible fibers, and then drying. Further, it can be obtained by spraying or coating a carboxyl-containing water-soluble binder and an aqueous solution containing water-soluble salt of at least one selected from the group consisting of an alkaline earth metal, manganese, zinc, cobalt and nickel, and then drying.

When the essential metallic ion is incorporated in the water-disintegrable paper in the form (A) above, namely a form of an intermolecular mixed salt of the water-soluble binder, the water-disintegrable paper is obtained by adding the intermolecular mixed salt binder into an aqueous dispersion of water-dispersible fibers and then subjecting paper making, or by spraying or coating a solution of the intermolecular mixed salt binder to a web composed of water-dispersible fibers and then drying.

Further, when the essential metallic ion is incorporated in the water-disintegrable paper in combination of forms (A) and (B) above, the above-mentioned incorporating processes are optionally combined to obtain the paper.

Processes for producing the water-disintegrable cleaning sheet of the present invention are not particularly restricted, and it can be produced, for example, by incorporating or impregnating an aqueous cleaning agent into the water-disintegrable paper as described above, or adding an aqueous cleaning agent into the water-disintegrable paper at any step of the above-mentioned production procedure of the water-disintegrable paper. Further, the water-disintegrable cleaning sheet can be produced by incorporating an aqueous cleaning agent together with the essential metallic ion of the present invention. In such production, the essential metallic ion is, for example, incorporated into the water-disintegrable cleaning sheet by dissolving at least one of water-soluble salt of the essential metallic ion, namely the form (B) as mentioned above, into an aqueous cleaning agent containing an organic solvent, and impregnating or spraying the resulting aqueous cleaning agent into the web containing carboxyl-containing water-soluble binder, and then drying.

The aqueous cleaning agent which is incorporated in the cleaning sheet essentially contains an organic solvent for obtaining high strength withstanding cleaning work. Suitable organic solvents are water-compatible (or water-soluble) solvents typically including monohydric lower alcohols such as ethanol, methanol, and propanol; glycols such as ethylene glycol, diethylene glycol, polyethylene glycol, propylene glycol, dipropylene glycol, butylene glycol and hexylene glycol; mono- or diethers of the aforementioned glycols and lower alcohols such as methanol, ethanol and butanol; esters of the aforementioned glycols and lower fatty acids; and polyhydric alcohols such as glycerine and sorbitol. In using water-insoluble solvents, they are added in the form of an emulsion.

The aqueous cleaning agent is usually used in an amount about 0.5 to 5 times, preferably 1 to 2.5 times the weight of water-disintegrable paper.

The content of the organic solvent in the aqueous cleaning agent ranges from 95 to 5% by weight, preferably from 8 to 92% by weight, and that of water ranges from 5 to 95% by weight, preferably from 92 to 8% by weight. For sterilization of toilet equipment, etc., cleaning agents rich in organic solvent, e.g., ethanol and isopropyl alcohol, are employed. For removal of hydrophilic dirt from living rooms, kitchens or toilet rooms, aqueous cleaning agents rich in water are employed. In this case, the water content ranges from 30 to 95% by weight, preferably from 40 to 92% by weight, more preferably from 60 to 90% by weight, and the organic solvent content ranges from 5 to 70% by weight, preferably from 8 to 60% by weight, more preferably from 10 to 40% by weight.

If desired, the aqueous cleaning agents may further contain surfactants, sterilizers, deodorizers; perfumes, and the like.

As the surfactants which may be contained in the cleaning agent of the present invention, anionic surfactants, nonionic surfactants, cationic surfactants and amphoteric surfactants are included. Preferred examples thereof include amine oxides having one or two of alkyl group containing 8 to 22 carbon atoms or

lower alkyl group, sulfobetaines or hydroxysulfobetaines having alkyl group containing 8 to 22 carbon atoms, and carbobetaines having alkyl group containing 8 to 22 carbon atoms, as amphoteric surfactants; alkylsulfates containing 8 to 22 carbon atoms, alkyl ether sulfates adding 1 to 30 mol of ethylene oxide and having alkyl group containing 8 to 22 carbon atoms, alkylbenzene sulfonic acid salts having alkyl group containing 8 to 22 carbon atoms, α -sulfofatty acid ester salts containing 8 to 22 carbon atoms, alkyl (or alkenyl) succinates containing 6 to 22 carbon atoms, and paraffinsulfonates containing 8 to 22 carbon atoms, as anionic surfactants; polyoxyalkylenes (mainly, polyoxyethylene, polyoxypropylene, or a mixture of these), glycol ethers, polyoxyalkylene alkyl phenyl ethers, alkyl glycosides, and sucrose fatty acid esters, as nonionic surfactants; quaternary ammonium salts having an alkyl group containing 8 to 14 carbon atoms, as cationic surfactants. These surfactants are added into the cleaning agents to be incorporate into water-disintegrable cleaning sheet in an amount of generally from 0.1 to 5% by weight.

A cleaning sheet prepared by simply impregnating water-disintegrable paper containing a carboxyl-containing water-soluble binder with an aqueous solution having dissolved therein the above-described metallic ion, or by simply incorporating the web composed of water-dispersible fibers with an intermolecular mixed salt of the water-soluble binder fails to exhibit sufficient strength enough to carry out cleaning. It is considered that a combined use of an organic solvent markedly accelerates formation of an insolubilized crosslinked complex of the water-soluble binder and the metallic ion to thereby afford sufficient strength for cleaning work even in using an aqueous cleaning agent having a very high water content. Further, when spent water-disintegrable paper is discarded into toilet flushing water, etc., the metallic ion and organic solvent in the sheet are diluted with a large quantity of water to make the insolubilized binder water-soluble, thereby maintaining water disintegrability.

As described above, the water-disintegrable cleaning sheet of the present invention, even when using a cleaning agent of high water content, exhibits strength withstanding cleaning work and satisfactory water disintegrability in good balance and produces great effects as cleaning sheet.

The present invention is now illustrated in greater detail by way of the following Examples, but it should be understood that the present invention is not construed as being limited thereto. All the percents, parts, and ratios are given on a weight basis unless otherwise indicated.

EXAMPLE 1

A toilet paper-like water-disintegrable paper sheet having a basis weight of 25 g/m² was produced from a bleached kraft pulp of conifer beaten to a CSF (Canadian Standard Freeness) of 680 cc using an ordinary paper machine.

The water-disintegrable paper sheet was sprayed with 3% (corresponding to 0.75 g/m²) of a sodium carboxymethyl cellulose "CMC 2200" (produced by Daisel Kagaku K.K.) in the form of a 1% aqueous solution and dried to obtain a CMC-containing sheet.

The CMC-containing sheet was impregnated with 1.7 times the sheet weight of a 1% solution of calcium chloride in an ethanol/water mixed solvent having a ratio of 50/50, 20/80, 10/90 or 0/100 to obtain a water-disintegrable cleaning sheet.

Wet tensile strength, dusting and fuzzing on use, and water disintegrability of the resulting cleaning sheet were evaluated in accordance with the following test methods. The results obtained are shown in Table 1 below.

1. Wet Tensile Strength:

A strip 25 mm wide and 100 mm long was cut out of the cleaning sheet, and breaking strength of the strip in the machine direction (MD) and cross direction (CD) was measured using a universal testing machine "RTM-25" (manufactured by Orientic K.K.) under conditions of 300 mm/min in rate of pulling and 50 mm in grip distance.

2. Dusting and Fuzzing:

The cleaning sheet was used for wiping black tiles inclusive of the joints for 5 minutes. Dusting on the tiles and fuzzing of the sheet are observed and evaluated according to the following rating system.

- : Neither substantial dusting nor fuzzing was observed.
- △: Slight dusting was observed, but fuzzing was not observed.
- X: Dusting and fuzzing were observed.

3. Water Disintegrability

In 1 l-volume beaker was put 500 ml of water and agitated with a stirrer at 300 rpm.

The cleaning sheet was cut to pieces of 50 mm x 50 mm and put into the water under stirring. After 90 seconds, the disintegrated and dispersed state of the sheet was observed and evaluated according to the following rating system, taking commercially available toilet paper as a standard having satisfactory dispersibility.

- o: Satisfactory dispersion
- Δ: Slightly poor dispersion
- X: Poor dispersion

COMPARATIVE EXAMPLE 1

A cleaning sheet was produced in the same manner as in Example 1, except for using an impregnating solution containing no calcium chloride. The resulting cleaning sheet was evaluated in the same manner as in Example 1, and the results obtained are shown in Table 1 below.

TABLE 1

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Example 1		Ethanol/Water (w/w)							
		50/50		20/80		10/90		0/100	
	Wet Tensile Strength (g/25mm)	MD 1020	CD 620	MD 480	CD 310	MD 370	CD 220	MD 40	CD 26
	Dusting and Fuzzing		○		○		○		×
	Water-Disintegrability		○		○		○		○

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Comparative Example 1									
	Wet tensile Strength (g/25mm)	MD 350	CD 200	MD 90	CD 50	MD 35	CD 20	MD 30	CD 17
	Dusting and Fuzzing		Δ		×		×		×
	Water-Disintegrability		○		○		○		○

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EXAMPLE 2

Each of calcium chloride, barium chloride, strontium nitrate, chromium chloride, manganese sulfate, zinc chloride, cobalt chloride, nickel nitrate, and lead sulfate was dissolved in a 2/8 mixed solvent of ethanol and water to prepare a 1% impregnating solution. The CMC-containing sheet as prepared in Example 1 was impregnated with a 1.7 times the sheet weight of the impregnating solution.

Each of the resulting water-disintegrable cleaning sheets was evaluated in the same manner as in Example 1, and the results obtained are shown in Table 2 below.

COMPARATIVE EXAMPLE 2

A cleaning sheet was produced in the same manner as in Example 2, except for replacing the metallic salt as used in Example 2 with potassium chloride, copper sulfate, ferrous chloride, ferric chloride, stannous chloride, or aluminum sulfate.

Each of the resulting sheets was evaluated in the same manner as in Example 1, and the results obtained are shown in Table 2 below.

TABLE 2

	<u>Metallic Ion in Solution</u>	<u>Wet Tensile Strength (g/25mm)</u>		<u>Dusting and Fuzzing</u>	<u>Water Disinte- grability</u>
		<u>MD</u>	<u>CD</u>		
	<u>Example 2</u>				
	Ca ²⁺	480	310	o	o
	Sr ²⁺	492	322	o	o
	Ba ²⁺	524	340	o	o
	Mn ²⁺	273	163	o	o
	Zn ²⁺	472	302	o	o
	Co ²⁺	396	194	o	o
	Ni ²⁺	440	276	o	o
	<u>Comparative Example 2</u>				
	K ⁺	42	19	x	o
	Cu ²⁺	540	348	o	x
	Fe ²⁺	442	283	o	x
	Sn ²⁺	480	320	o	x
	Fe ³⁺	686	390	o	x
	Al ³⁺	760	411	o	x

EXAMPLE 3

Calcium chloride was dissolved in a 2/8 mixed solvent of ethanol and water in a prescribed concentration, and the resulting impregnating solution was impregnated into the CMC-containing sheet as prepared in Example 1 in an amount of 1.7 times the weight of the sheet to obtain a water-disintegrable cleaning sheet containing a Ca²⁺ ion at a molar ratio of 1/4, 1/2, or 1/1 to the carboxylate ion of CMC.

Each of the resulting cleaning sheets was evaluated in the same manner as in Example 1, and the results obtained are shown in Table 3 below.

TABLE 3

Ca ²⁺ /COO ⁻ Molar Ratio	Wet Tensile Strength (g/25mm)		Dusting and Fuzzing	Water Disintegrability
	MD	CD		
1/1	560	310	o	o
1/2	490	290	o	o
1/4	345	190	o	o

EXAMPLE 4

A web of split and deposited fibers of a conifer fluff pulp (basis weight: 30 g/m²) was sprayed with 15% of a sodium salt of an acrylic acid-2-ethylhexyl acrylate copolymer (7/3 by mol), followed by drying to obtain a water-soluble binder-containing water-disintegrable sheet.

The resulting sheet was impregnated with 1.5 times the sheet weight of an aqueous cleaning agent comprising zinc sulfate, polyoxyethylene dodecyl ether (p=8), propylene glycol and water at a ratio of 1/1/15/83 to obtain a water-disintegrable cleaning sheet.

The resulting cleaning sheet was evaluated in the same manner as in Example 1, and the results obtained are shown in Table 4 below.

COMPARATIVE EXAMPLE 3

The water-soluble binder-containing water-disintegrable sheet as prepared in Example 4 was impregnated with an aqueous cleaning agent comprising polyoxyethylene dodecyl ether (p=8), propylene glycol, and water at a ratio of 1/15/84 in the same manner as in Example 4.

The resulting cleaning sheet was evaluated in the same manner as in Example 1, and the results obtained are shown in Table 4 below.

TABLE 4

Example No.	Wet Tensile Strength (g/25mm)		Dusting and Fuzzing	Water Disintegrability
	MD	CD		
Example 1	260	280	o	o
Comparative Example 3	15	13	x	o

EXAMPLE 5

Crepe paper having a basis weight of 25 g/m² (crepe ratio: 20%) was produced from a raw material comprising 100 parts of parts of NBKP (softwood kraft pulp) and 10 part of CMC2200 using a cylindrical net-Yankee machine.

The resulting CMC-containing sheet was sprayed with 1 part of a 2% calcium chloride aqueous solution per part of the sheet and dried to obtain a water-disintegrable sheet.

The sheet was impregnated with 1.5 times the sheet weight of a cleaning agent comprising a surfactant (Softanol 70), ethanol, and water (1/20/79). The resulting cleaning sheet was evaluated in the same manner as in Example 1, and the results obtained are shown in Table 5 below.

COMPARATIVE EXAMPLE 4

The CMC-containing crepe paper as described in Example 5 was impregnated with 1.5 times the paper weight of the same cleaning agent as used in Example 5. The resulting cleaning sheet was evaluated in the same manner as in Example 1, and the results obtained are shown in Table 5 below.

TABLE 5

	<u>Example 5</u>	<u>Comparative Example 4</u>
Wet Tensile Strength (g/25 mm):		
MD	520	50
CD	300	30
Dusting	o	x
Water Disintegrability	o	o

EXAMPLE 6

Toilet paper-like crepe paper having a basis weight of 20 g/m² (crepe ratio: 10%) was produced from a raw material comprising 60 parts of NBKP and 40 parts of LBKP (broad-leaved tree kraft pulp) using a cylindrical net-Yankee machine.

The crepe paper was coated with 3% the paper weight of CMC2200 with a gravure coater followed by drying to obtain CMC-containing paper.

The CMC-containing paper was uniformly sprayed with part of a 2% aqueous solution of zinc sulfate per part of the paper and dried to obtain water-disintegrable paper.

The resulting water-disintegrable paper was impregnated with 2.0 times the paper weight of a cleaning agent comprising a surfactant (polyoxyethylene dodecyl ether ($\bar{p}=12$)), propylene glycol, and water (2/15/83), and the properties of the impregnated paper were evaluated in the same manner as in Example 1. The results obtained are shown in Table 6 below.

COMPARATIVE EXAMPLE 5

The CMC-containing paper as prepared in Example 6 was impregnated with the same cleaning agent as used in Example 6. The impregnated paper was evaluated in the same manner as in Example 1, and the results obtained are shown in Table 6 below.

EXAMPLE 7

The crepe paper as described in Example 6 was coated with 3% the paper weight of a 3:1 mixture of CMC2200 and calcium chloride with a gravure coater and dried to obtain water-disintegrable paper.

The water-disintegrable paper was impregnated with 2.0 times the paper weight of the same cleaning agent as used in Example 6. The impregnated paper was evaluated in the same manner as in Example 1, and the results are shown in Table 6 below.

TABLE 6

		<u>Example 6</u>	<u>Example 7</u>	<u>Comparative Example 5</u>
5	Wet Tensile Strength (g/25mm):			
	MD	480	420	55
	CD	350	300	40
10	Dusting	o	o	x
	Water Disintegrability	o	o	o

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EXAMPLE 8

20 A web of split and deposited fibers of conifer fluff pulp (basis weight: 40 g/m²) was sprayed with 15% the weight of a 3:2 mixture of CMC1330 (produced by Daisel K.K.) and calcium chloride and dried to obtain water-disintegrable paper.

The water-disintegrable paper was impregnated with 3 times the paper weight of a cleaning agent comprising polyethylene dodecyl ether ($\bar{p}=10$), ethylene glycol and water (1/19/80), and the properties of the impregnated paper were evaluated in the same manner as in Example 1. The results obtained are shown in Table 7 below.

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COMPARATIVE EXAMPLE 6

30 The web as described in Example 8 was sprayed with 10% the web weight of CMC1330 and dried. The resulting CMC-containing paper was impregnated with a cleaning agent in the same manner as in Example 8. The properties of the impregnated paper are shown in Table 7.

TABLE 7

		<u>Example 8</u>	<u>Comparative Example 6</u>
35	Wet Tensile Strength (g/25 mm):		
40	MD	320	18
	CD	310	20
	Dusting	o	x
45	Water Disintegrability	o	o

50 EXAMPLE 9

The crepe paper as described in Example 6 was coated with 3% the paper weight of a monoethanolamine salt of a methacrylic acid-lauryl methacrylate copolymer (7/3 by mol) with a gravure coater and dried to obtain water-soluble binder-containing paper.

55 The paper was uniformly sprayed with 1 part of a 2% calcium chloride aqueous solution per part of the paper and dried to obtain water-disintegrable paper.

The water-disintegrable paper was impregnated with 1.5 times the paper weight of a cleaning agent comprising a surfactant (dodecyldimethylamine oxide), polyethylene glycol 400 and water (1/20/79). Prop-

erties of the impregnated paper were evaluated in the same manner as in Example 1, and the results obtained are shown in Table 8 below.

COMPARATIVE EXAMPLE 7

The water-soluble binder-containing paper as obtained in Example 9 was impregnated with a cleaning agent in the same manner as in Example 9. Properties of the impregnated paper are shown in Table 8 below.

TABLE 8

		<u>Example 9</u>	<u>Comparative Example 7</u>
	Wet Tensile Strength (g/25 mm):		
	MD	450	48
	CD	310	40
	Dusting	o	x
	Water Disintegrability	o	o

EXAMPLE 10

Water-disintegrable crepe paper having a basis weight of 25 g/m² (crepe ratio: 15%) was produced from a raw material comprising 100 parts of NBKP and 10 parts of a water-soluble carboxymethyl cellulose sodium-calcium mixed salt (Na:Ca = 1/1 by mol; produced by Daisel K.K.) using a cylindrical net-Yankee machine.

The water-disintegrable paper was impregnated with 1.7 times the paper weight of a cleaning agent comprising a surfactant (Softanol 90), ethanol and water (1/15/84), and the impregnated paper was evaluated in the same manner as in Example 1. The results obtained are shown in Table 9 below.

COMPARATIVE EXAMPLE 8

Water-disintegrable crepe paper having a basis weight of 25 g/m² (crepe ratio: 15%) was produced from a raw material comprising 100 parts of NBKP and 10 parts of a water-soluble sodium carboxymethyl cellulose (produced by Daisel K.K.) using a cylindrical net-Yankee machine.

The water-disintegrable paper was impregnated with a cleaning agent in the same manner as in Example 10. Properties of the impregnated paper are shown in Table 9.

TABLE 9

		<u>Example 10</u>	<u>Comparative Example 8</u>
	Wet Tensile Strength (g/25 mm):		
	MD	300	45
	CD	250	25
	Dusting	o	x
	Water Disintegrability	o	o

EXAMPLE 11

Toilet paper-like crepe paper having a basis weight of 20 g/m² (crepe ratio: 10%) was produced from a raw material comprising 70 parts of NBKP and 30 parts of LBKP using a cylindrical net-Yankee machine.

5 The crepe paper was coated with 3% the paper weight of a water-soluble carboxymethyl cellulose sodium-zinc mixed salt (Na:Zn=10/1 by mol; produced by Daisel K.K.) and dried to obtain water-disintegrable paper.

10 The water-disintegrable paper was impregnated with 2.0 times the paper weight of a cleaning agent comprising a surfactant (polyoxyethylene dodecyl ether ($\bar{p}=12$)), propylene glycol and water (2/15/83). The impregnated paper was evaluated in the same manner as in Example 1, and the results obtained are shown in Table 10 below.

COMPARATIVE EXAMPLE 9

15 The crepe paper as described in Example 11 was coated with 3% the paper weight of a water-soluble sodium carboxymethyl cellulose with a gravure coater and dried to obtain water-disintegrable paper.

The water-disintegrable paper was impregnated with a cleaning agent in the same manner as in Example 11. Properties of the impregnated paper are shown in Table 10.

EXAMPLE 12

20 The crepe paper as described in Example 11 was coated with 3% the paper weight of a water-soluble carboxymethyl cellulose sodium-calcium mixed salt (Na:Ca=10/1 by mol; produced by Daisel K.K.) and dried to obtain water-disintegrable paper.

25 The water-disintegrable paper was impregnated with 2.0 times the paper weight of a cleaning agent comprising surfactant, propylene glycol and water. The impregnated paper was evaluated in the same manner as in Example 1, and the results obtained are shown in Table 10 below.

TABLE 10

		Comparative		
		<u>Example 11</u>	<u>Example 12</u>	<u>Example 9</u>
35	Wet Tensile Strength (g/25 mm):			
	MD	320	470	40
	CD	250	350	20
40	Dusting	o	o	x
	Water Disintegrability	o	o	o

EXAMPLE 13

45 A web of split and deposited fibers of conifer fluff pulp having a basis weight of 40 g/m² was sprayed with 10% the web weight of a water-soluble carboxymethyl cellulose sodium-calcium mixed salt (Na:Ca=1/1 by mole) and dried to obtain water-disintegrable paper.

50 The water-disintegrable paper was impregnated with 3 times the paper weight of a cleaning agent comprising a surfactant (polyethylene dodecyl ether ($\bar{p}=10$)), ethylene glycol and water (1/19/80). The impregnated paper was evaluated in the same manner as in Example 1, and the results obtained are shown in Table 11 below.

55

COMPARATIVE EXAMPLE 10

The web as described in Example 13 was sprayed with 10% the web weight of a water-soluble sodium carboxymethyl cellulose and dried to obtain water-disintegrable paper.

5 The water-disintegrable paper was impregnated with a cleaning agent in the same manner as in Example 13. Properties of the impregnated paper are shown in Table 11.

TABLE 11

10		<u>Example 13</u>	<u>Comparative Example 10</u>
	Wet Tensile Strength (g/25 mm):		
15	MD	310	10
	CD	280	15
	Dusting	o	x
20	Water Disintegrability	o	o

25 EXAMPLE 14

The crepe paper as described in Example 11 was coated with 3% the paper weight of a water-soluble methacrylic acid-lauryl methacrylate copolymer (7/3 by mol) potassium-calcium mixed salt (K:Ca = 1/1 by mole) with a gravure coater and dried to obtain water-disintegrable paper.

30 The water-disintegrable paper was impregnated with 1.5 times the paper weight of a cleaning agent comprising a surfactant (dodecyltrimethylamine oxide), polyethylene glycol 400 and water (1/19/80), and the impregnated paper was evaluated in the same manner as in Example 1. The results obtained are shown in Table 12 below.

35 COMPARATIVE EXAMPLE 11

The crepe paper as described in Example 11 was coated with 3% of a methacrylic acid-lauryl methacrylate copolymer (7/3 by mol) sodium salt and dried to obtain water-soluble binder-containing paper.

40 The water-soluble binder-containing paper was impregnated with a cleaning agent in the same manner as in Example 14. Properties of the impregnated paper are shown in Table 12 below.

TABLE 12

45		<u>Example 14</u>	<u>Comparative Example 11</u>
	Wet Tensile Strength (g/25 mm):		
50	MD	410	36
	CD	280	25
	Dusting	o	x
55	Water Disintegrability	o	o

EXAMPLE 15

A water-disintegrable paper sheet having a basis weight of 25 g/m² was produced from a bleached kraft pulp of conifer beaten to a CSF (Canadian Standard Freeness) of 680 cc using an ordinary paper machine.

5 The water-disintegrable paper sheet was sprayed with 3% the paper weight (corresponding to 0.75 g/m²) of a sodium carboxymethyl cellulose "CMC 1330" (produced by Daisel Kagaku K.K.) in the form of a 1% aqueous solution and dried to obtain a CMC-containing sheet.

Separately, the water-disintegrable paper sheet was sprayed with 3% the paper weight (corresponding to 0.75 g/m²) of a sodium polyacrylate having a mean molecular weight of 135,000 (produced by Aldrich Chemical Company, Inc.) in the form of a 1% aqueous solution and dried to obtain a polyacrylate-containing sheet.

The CMC-containing sheet and the polyacrylate-containing sheet were impregnated with 1.7 times the sheet weight of a cleaning agent comprising calcium chloride, polyoxyethylene dodocylether ($\bar{p}=8$), ethanol and water (1/1/20/78) to obtain a water-disintegrable cleaning sheet.

15 Wet tensile strength, dusting and fuzzing on use, and water disintegrability of the resulting cleaning sheet were evaluated in accordance with the following test methods. The results obtained are shown in Table 13 below.

1. Wet Tensile Strength:

20 The same as in Example 1.

2. Dusting and Fuzzing:

25 The same as in Example 1.

3. Water Disintegrability:

In 1 l-volume beaker was put 500 ml of tap water and a Teflon coated stirrer bar, and agitated by means of a magnetic stirrer at 300 rpm.

The cleaning sheet was cut to pieces of 50 mm x 50 mm and put into the water under stirring. The time required for collapse (water disintegration) of the sheet in water was measured.

COMPARATIVE EXAMPLE 12

35 The water-disintegrable paper sheet as described in Example 15 was sprayed with 3% the paper weight (corresponding to 0.75 g/m²) of carrageenan having a mean molecular weight of 300,000 (produced by Tokyo Kasei K.K.) in the form of a 1% aqueous solution and dried to obtain a carrageenan-containing sheet.

40 The carrageenan-containing sheet was impregnated with a cleaning agent in the same manner as in Example 15. Properties of the impregnated paper are shown in Table 13 below.

	<u>TABLE 13</u>			
	<u>Wet Tensile</u>		<u>Dusting</u>	<u>Water</u>
	<u>Strength (g/25mm)</u>		<u>and</u>	<u>Disinte-</u>
	<u>MD</u>	<u>CD</u>	<u>Fuzzing</u>	<u>grability</u>
				<u>(sec.)</u>
45	<u>Example 15</u>			
	CMC-containing Sheet	430 270	o	14
50	Polyacrylic acid-containing Sheet	620 390	o	45
	<u>Comparative Example 12</u>			
55	Carrageenan-containing Sheet	78 46	Δ	17

Claims

1. A water-disintegrable cleaning sheet comprising a web of water-dispersible fibers having incorporated thereinto a water-soluble binder having a carboxyl group; at least one metallic ion selected from the group consisting of ions of alkaline earth metals, manganese, zinc, cobalt, and nickel; and an aqueous cleaning agent containing an organic solvent.
2. The water-disintegrable cleaning sheet as claimed in Claim 1, wherein said water-soluble binder is an alkali metal salt formed between the carboxyl group thereof and an alkali metal.
3. The water-disintegrable cleaning sheet as claimed in Claim 1, wherein said at least one metallic ion selected from the group consisting of ions of alkaline earth metals, manganese, zinc, cobalt, and nickel, is incorporated thereinto in the forms of:
 - (A) an intermolecular mixed salt of said water-soluble binder formed between the carboxyl group thereof and (a) an alkali metal and (b) at least one selected from the group consisting of alkaline earth metals, manganese, zinc, cobalt and nickel; and/or
 - (B) a water-soluble salt.
4. The water-disintegrable cleaning sheet as claimed in Claim 3, wherein a molar ratio of (a) an alkali metal and (b) at least one polyvalent metal selected from the group consisting of alkaline earth metals, manganese, zinc, cobalt, and nickel, of said intermolecular mixed salt (A) is in the ranges from 1/0.01 to 1/10.
5. The water-disintegrable cleaning sheet as claimed in Claim 3, wherein said water-soluble salt is at least one selected from the group consisting of a hydroxide, a chloride, a sulfate, a nitrate, a carbonate, a formate and an acetate, of at least one selected from the group consisting of alkaline earth metals, manganese, zinc, cobalt, and nickel.
6. The water-disintegrable cleaning sheet as claimed in Claim 1, wherein said water-soluble binder is present in a amount of from 0.1 to 30% by weight based on the dry weight of the web.
7. The water-disintegrable cleaning sheet as claimed in Claim 1, wherein an amount of said at least one metallic ion selected from the group consisting of ions of alkaline earth metals, manganese, zinc, cobalt, and nickel, is at least 1/4 mol per mol of the carboxyl group of said water-soluble binder.
8. The water-disintegrable cleaning sheet as claimed in Claim 1, wherein said water-soluble binder is a carboxymethyl cellulose.
9. The water-disintegrable cleaning sheet as claimed in Claim 1, wherein said water-soluble binder is a polymer of an unsaturated carboxylic acid, a copolymer of two or more of an unsaturated carboxylic acid, or a copolymer of an unsaturated carboxylic acid and other copolymerizable monomer.
10. The water-disintegrable cleaning sheet as claimed in Claim 9, wherein said unsaturated carboxylic acid is acrylic acid or methacrylic acid.
11. The water-disintegrable cleaning sheet as claimed in Claim 1, wherein said organic solvent contained in said aqueous cleaning agent is a water compatible solvent.
12. The water-disintegrable cleaning sheet as claimed in Claim 1, wherein said aqueous cleaning agent is containing said organic solvent in an amount ranges from 5 to 95% by weight, and water in an amount ranges from 95 to 5% by weight.

Patentansprüche

1. Ein im Wasser abbaubares Reinigungsblatt, das ein Gewebe aus wasserdispergierbaren Fasern umfaßt, wobei hierin ein wasserlösliches Bindemittel mit einer Carboxylgruppe; mindestens ein Metallion aus der Reihe der Ionen von Erdalkalimetallen, Mangan, Zink, Kobalt und Nickel; und ein organisches Lösungsmittel enthaltendes, wäßriges Reinigungsmittel eingearbeitet sind.

2. Das im Wasser abbaubare Reinigungsblatt nach Anspruch 1, wobei das wasserlösliche Bindemittel ein Alkalimetallsalz ist, das zwischen der Carboxylgruppe hiervon und einem Alkalimetall gebildet ist.
3. Das im Wasser abbaubare Reinigungsblatt nach Anspruch 1, wobei das mindestens eine Metallion, ausgewählt aus der Reihe der Ionen von Erdalkalimetallen, Mangan, Zink, Kobalt und Nickel, hierin in Form
(A) eines intermolekularen Mischsalzes des wasserlöslichen Bindemittels, das zwischen der Carboxylgruppe hiervon und (a) einem Alkalimetall und (b) mindestens einem Metall, ausgewählt aus Erdalkalimetallen, Mangan, Zink, Kobalt und Nickel, gebildet ist; und/oder
(B) eines wasserlöslichen Salzes eingearbeitet ist.
4. Das im Wasser abbaubare Reinigungsblatt nach Anspruch 3, wobei das molare Verhältnis von (a) einem Alkalimetall und (b) mindestens einem mehrwertigen Metall, ausgewählt aus der Reihe Erdalkalimetalle, Mangan, Zink, Kobalt und Nickel, in dem intermolekularen Mischsalz (A) im Bereich von 1/0,01 bis 1/10 liegt.
5. Das im Wasser abbaubare Reinigungsblatt nach Anspruch 3, wobei das wasserlösliche Salz mindestens ein Salz, ausgewählt aus einem Hydroxid, Chlorid, Sulfat, Nitrat, Carbonat, Formiat und Acetat, von mindestens einem Metall, ausgewählt aus Erdalkalimetallen, Mangan, Zink, Kobalt und Nickel, ist.
6. Das im Wasser abbaubare Reinigungsblatt nach Anspruch 1, wobei das wasserlösliche Bindemittel in einer Menge von 0,1 bis 30 Gew.% in bezug auf das Trockengewicht des Gewebes vorliegt.
7. Das im Wasser abbaubare Reinigungsblatt nach Anspruch 1, wobei die Menge des mindestens einen Metallions, ausgewählt aus der Reihe der Ionen von Erdalkalimetallen, Mangan, Zink, Kobalt und Nickel, mindestens 1/4 Mol pro Mol der Carboxylgruppe des wasserlöslichen Bindemittels beträgt.
8. Das im Wasser abbaubare Reinigungsblatt nach Anspruch 1, wobei das wasserlösliche Bindemittel eine Carboxymethylzellulose ist.
9. Das im Wasser abbaubare Reinigungsblatt nach Anspruch 1, wobei das wasserlösliche Bindemittel ein Polymer einer ungesättigten Carbonsäure, ein Copolymer von zwei oder mehreren ungesättigten Carbonsäuren, oder ein Copolymer von einer ungesättigten Carbonsäure und einem anderen copolymerisierbaren Monomer ist.
10. Das im Wasser abbaubare Reinigungsblatt nach Anspruch 9, wobei die ungesättigte Carbonsäure Acrylsäure oder Methacrylsäure ist.
11. Das im Wasser abbaubare Reinigungsblatt nach Anspruch 1, wobei das in dem wässrigen Reinigungsmittel enthaltene organische Lösungsmittel ein wasserkompatibles Lösungsmittel ist.
12. Das im Wasser abbaubare Reinigungsblatt nach Anspruch 1, wobei das wässrige Reinigungsmittel das organische Lösungsmittel in einer Menge von 5 bis 95 Gew.% und Wasser in einer Menge von 95 bis 5 Gew.% enthält.

Revendications

1. Feuille nettoyante désagrégeable dans l'eau comprenant un tissu de fibres dispersibles dans l'eau y ayant incorporé un liant hydrosoluble ayant un groupe carboxyle; au moins un ion métallique choisi dans le groupe constitué des ions des métaux alcalino-terreux, du manganèse, du zinc, du cobalt, et du nickel; et un agent nettoyant aqueux contenant un solvant organique.
2. Feuille nettoyante désagrégeable dans l'eau selon la revendication 1, dans laquelle ledit liant hydrosoluble est un sel de métal alcalin formé entre son groupe carboxyle et un métal alcalin.
3. Feuille nettoyante désagrégeable dans l'eau selon la revendication 1, dans laquelle ledit au moins un ion métallique choisi dans le groupe constitué des ions des métaux alcalino-terreux, du manganèse, du zinc, du cobalt, et du nickel, y est incorporé sous les formes:

(A) d'un sel mixte intermoléculaire dudit liant hydrosoluble entre son groupe carboxyle et (a) un métal alcalin et (b) au moins un métal choisi dans le groupe constitué des métaux alcalino-terreux, du manganèse, du zinc, du cobalt, et du nickel; et/ou
(B) d'un sel hydrosoluble.

- 5 4. Feuille nettoyante désagrégeable dans l'eau selon la revendication 3, dans laquelle un rapport molaire (a) d'un métal alcalin et (b) d'au moins un métal polyvalent choisi dans le groupe constitué des métaux alcalino-terreux, du manganèse, du zinc, du cobalt, et du nickel, dudit sel mixte intermoléculaire (A), est compris entre 1:0,01 et 1:10.
- 10 5. Feuille nettoyante désagrégeable dans l'eau selon la revendication 3, dans laquelle ledit sel hydrosoluble est au moins un sel choisi dans le groupe constitué d'un hydroxyde, d'un chlorure, d'un sulfate, d'un nitrate, d'un carbonate, d'un formiate et d'un acétate, d'au moins un métal choisi dans le groupe constitué des métaux alcalino-terreux, du manganèse, du zinc, du cobalt, et du nickel.
- 15 6. Feuille nettoyante désagrégeable dans l'eau selon la revendication 1, dans laquelle ledit liant hydrosoluble est présent en une quantité comprise entre 0,1 et 30% en poids par rapport au poids sec du tissu.
- 20 7. Feuille nettoyante désagrégeable dans l'eau selon la revendication 3, dans laquelle une quantité dudit au moins un ion métallique choisi dans le groupe constitué des ions des métaux alcalino-terreux, du manganèse, du zinc, du cobalt, et du nickel, est d'au moins 1/4 de mole par mole du groupe carboxyle dudit liant hydrosoluble.
- 25 8. Feuille nettoyante désagrégeable dans l'eau selon la revendication 1, dans laquelle ledit liant hydrosoluble est une carboxyméthylcellulose.
9. Feuille nettoyante désagrégeable dans l'eau selon la revendication 1, dans laquelle ledit liant hydrosoluble est un polymère d'un acide carboxylique insaturé, un copolymère de deux ou plusieurs acides carboxyliques insaturés, ou un copolymère d'un acide carboxylique insaturé et d'un autre monomère copolymérisable.
- 30 10. Feuille nettoyante désagrégeable dans l'eau selon la revendication 9, dans laquelle ledit acide carboxylique insaturé est l'acide acrylique ou l'acide méthacrylique.
- 35 11. Feuille nettoyante désagrégeable dans l'eau selon la revendication 1, dans laquelle ledit solvant organique contenu dans ledit agent nettoyant aqueux est un solvant compatible avec l'eau.
- 40 12. Feuille nettoyante désagrégeable dans l'eau selon la revendication 1, dans laquelle ledit agent nettoyant aqueux contient ledit solvant organique en une quantité comprise entre 5 et 95% en poids, et de l'eau en une quantité comprise entre 95 et 5% en poids.